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(54) **Carboxyalkyl polysaccharides and process for their preparation.**

(57) Disclosed is a method for producing a water-swellaable, generally water-insoluble, carboxyalkyl polysaccharide having improved absorption properties. The method involves forming a solution of carboxyalkyl polysaccharide and water, recovering the carboxyalkyl polysaccharide from the solution and heat-treating said recovered carboxyalkyl polysaccharide. Also, described is a carboxyalkyl polysaccharide having improved absorption properties.

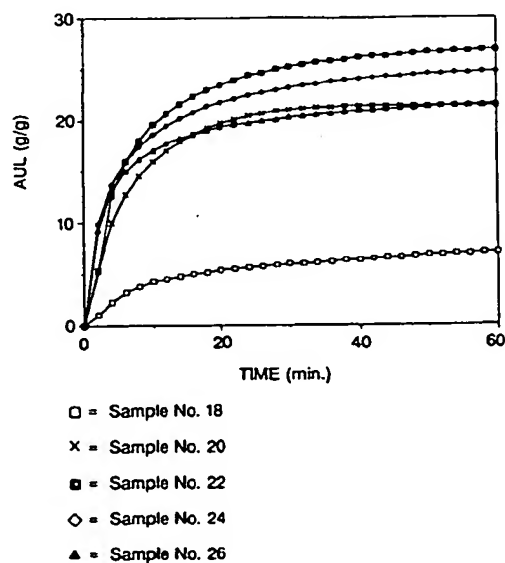


FIG. 2

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The present invention relates to carboxyalkyl polysaccharides having improved absorbent properties. Specifically, the present invention relates to carboxyalkyl polysaccharides having the ability to absorb liquid while under a load, and a process for the preparation thereof.

The use of absorbent materials, commonly known as superabsorbents, in disposable absorbent  
 5 personal care products is known. Such absorbent materials are generally employed in absorbent products such as diapers, training pants, adult incontinence products, feminine care products, and the like, in order to increase the absorbent capacity of such products while reducing their overall bulk. Such absorbent materials are generally present in absorbent products in a fibrous matrix, such as a matrix of wood pulp fluff. A matrix of wood pulp fluff generally has an absorbent capacity of about 6 grams of liquid per gram of  
 10 fluff. The absorbent materials described above generally have an absorbent capacity of at least about 10, preferably of about 20, and often of up to 100 times their weight in water. Clearly, incorporation of such absorbent materials in personal care products can reduce the overall bulk while increasing the absorbent capacity of such products.

A wide variety of materials have been described for use as absorbent materials in such personal care  
 15 products. Such materials include natural-based materials such as agar, pectin, gums, carboxyalkyl starch, carboxyalkyl cellulose, and the like, as well as synthetic materials such as polyacrylates, polyacrylamides, hydrolyzed polyacrylonitrile, and the like. While the natural-based, absorbent materials are known for use in personal care products, they have not gained wide usage in such products. The natural-based, absorbent materials have not gained wide usage in personal care products, at least in part, because their absorbent  
 20 properties are inferior compared to the synthetic absorbent materials such as the polyacrylates. Specifically, many of the natural-based materials tend to form soft, gelatinous masses when swollen with a liquid. When employed in absorbent products, the presence of such soft gelatinous masses tends to prevent the transport of liquid within the fibrous matrix in which the absorbent materials are incorporated. This phenomenon is known as gel-blocking. Once gel-blocking occurs, subsequent insults of liquid cannot be  
 25 efficiently absorbed by the product, and the product tends to leak. Further, many of the natural-based materials exhibit poor absorption properties, particularly when subjected to external pressures.

In contrast, the synthetic, absorbent materials are often capable of absorbing large quantities of liquid while maintaining a generally stiff, non-gelatinous character. Accordingly, the synthetic, absorbent materials can be incorporated in absorbent products while minimizing the likelihood of gel-blocking.

30 Carboxyalkyl cellulose materials and other carboxyalkyl polysaccharides are known in the art. As a general rule, carboxyalkyl cellulose materials are formed from a cellulosic material which has been treated with carboxyalkylating reactants such as a chloroalkanoic acid, preferably monochloroacetic acid, and an alkali, such as sodium hydroxide, optionally, in the presence of an alcohol. Such a process is described, for example, in U.S. Patent 3,723,413, issued March 27, 1973, to Chatterjee et al. Such carboxyalkyl celluloses  
 35 are generally water-soluble. Various methods of rendering such water-soluble carboxyalkyl celluloses water-insoluble are known.

U.S. Patent 2,639,239 issued May 19, 1953, to Elliott describes a process in which a commercially available water-soluble, alkali-metal salt of carboxymethyl cellulose having a degree of substitution of from about 0.5 to about 1 is subjected to a thermal treatment for up to 10 hours which renders such water-  
 40 soluble carboxymethyl cellulose capable of forming highly swollen gel particles.

Similarly, U.S. Patent 3,723,413, discussed above, describes the heat treatment of a carboxyalkyl cellulose in the presence of remaining carboxyalkylating reactants and by-products, such that the carboxyalkyl cellulose becomes water-insoluble and possessed of desirable liquid absorptive and retentive properties and characteristics.

45 U.S. Patent 3,379,720 issued April 23, 1968, to Reid describes a process of preparing modified polysaccharides such as ethers and esters of cellulose comprising slurrying a water-soluble polysaccharide in any inert medium, acidifying said polysaccharide, removing excess acid from the acidified polysaccharide, drying same and heat-curing.

U.S. Patent 4,689,408 issued August 25, 1987, to Gelman et al. describes a method of preparing salts  
 50 of carboxymethyl cellulose. The method involves treating a carboxymethyl cellulose with water, adding a nonsolvent for the carboxymethyl cellulose, and recovering the carboxymethyl cellulose. The carboxymethyl cellulose is said to have an absorbency of at least 25 grams of liquid per gram of carboxymethyl cellulose.

Unfortunately, the known carboxyalkyl polysaccharide materials do not possess absorptive properties comparable to many of the synthetic, highly absorptive materials. This has prevented widespread use of  
 55 such carboxyalkyl polysaccharides in absorbent personal care products.

It is desirable to develop and produce a natural-based, highly absorbent material having absorptive properties similar to the synthetic, highly absorptive materials and thus suitable for use in personal care absorbent products.

The present invention concerns a method for producing a water-swella-  
ble, water-insoluble carboxyalkyl polysaccharide. The method comprises the steps of forming a solution comprising a water-soluble  
carboxyalkyl polysaccharide and water. The carboxyalkyl polysaccharide has an average degree of  
substitution of from about 0.3 to about 1.5. The carboxyalkyl polysaccharide is recovered from said solution  
and heat-treated at a temperature and for a time sufficient to crosslink the carboxyalkyl polysaccharide.

The present invention further concerns a water-swella-  
ble, generally water-insoluble carboxyalkyl polysaccharide. The carboxyalkyl polysaccharide is characterized in that it has an average degree of substitu-  
tion of from about 0.3 to about 1.5, that it has an Absorbency Under Load of at least about 17 and a Free-  
Swell Capacity of at least about 20 grams per gram.

Fig. 1 illustrates the apparatus for determining the Absorbency Under Load values of an absorbent  
material.

Figs. 2-10 illustrate, in the form of graphs, the results of the physical property testing set forth in Tables  
1-5.

In one aspect, the present invention concerns a method for producing a water-swella-  
ble, water-insoluble carboxyalkyl polysaccharide. The method comprises the steps of forming a solution comprising carboxy-  
alkyl polysaccharide and water. The carboxyalkyl polysaccharide is recovered from the solution and heat-  
treated for a time and at a temperature sufficient to crosslink the carboxyalkyl polysaccharide.

Suitable carboxyalkyl polysaccharides for use in the present invention include carboxyalkyl cellulose  
such as carboxymethyl cellulose, carboxyethyl cellulose, carboxyalkyl carageenan, carboxyalkyl agar,  
carboxyalkyl gellan gum, and the like, and mixtures thereof. The preferred carboxyalkyl polysaccharide is a  
carboxyalkyl cellulose with the preferred carboxyalkyl cellulose being carboxymethyl cellulose. While any  
carboxyalkyl polysaccharide is believed suitable for use in the present invention, carboxyalkyl cellulose is  
preferred. Accordingly, the preferred embodiments discussed below will be described in the context of  
using carboxyalkyl cellulose as the carboxyalkyl polysaccharide. However, it is to be understood that other  
suitable carboxyalkyl polysaccharides can be used.

Methods of making carboxyalkyl cellulose are known to those skilled in the art. Suitably, a cellulosic  
material such as wood pulp fluff, cotton, cotton linters, and the like are provided. The cellulosic material  
may be in the form of fibers or of fibers which have been comminuted to particulate form. The cellulosic  
material is dispersed in an inert solvent such as an alcohol and carboxyalkylating reagents added to the  
dispersion. Carboxyalkylating reagents generally comprise a chloroalkanoic acid such as monochloroacetic  
acid and sodium hydroxide.

It is to be understood that it may be possible to perform the carboxyalkylation of the starting  
polysaccharide in such a manner that the solution of carboxyalkyl cellulose and water is formed directly.  
That is, the carboxyalkylation process may be performed in an aqueous medium such that, upon formation  
of the carboxyalkyl cellulose, it is solubilized in the water. In this manner, no recovery step is necessary  
between formation of the carboxyalkyl cellulose and the formation of the solution of carboxyalkyl cellulose  
and water.

The carboxyalkyl celluloses suitable for use in the present invention generally have an average degree  
of substitution from about 0.3 to about 1.5, preferably from about 0.4 to about 1.2. The degree of  
substitution refers to the average number of carboxyl groups present on the anhydroglucose unit of the  
cellulosic material. When the carboxyalkyl celluloses have an average degree of substitution within the  
range of from about 0.3 to about 1.5, the carboxyalkyl cellulose is generally water-soluble.

As used herein, a carboxyalkyl cellulose will be considered to be water-soluble when it either dissolves  
in water to form a true solution, or swells in water to a large extent even though a true solution may not be  
formed.

Carboxyalkyl cellulose is available in a wide range of molecular weights. Carboxyalkyl cellulose having  
a relatively high molecular weight is desired for use in the present invention. It is generally most convenient  
to express the molecular weight of a carboxyalkyl cellulose in terms of its viscosity in a 2.0 weight percent  
aqueous solution. Carboxymethyl celluloses suitable for use in the present invention will generally have a  
viscosity in a 2.0 weight percent aqueous solution of from about 50 mPa's (CP) to about 80,000 mPa's  
preferably from about 2,000 to about 80,000 mPa's, and most preferably from about 20,000 to about 80,000  
mPa's.

Suitable carboxyalkyl celluloses are commercially available from numerous vendors. Exemplary of a  
commercially available carboxyalkyl cellulose is carboxymethyl cellulose, commercially available from  
Aqualon Company under the trade designation Aqualon™ or Blanose™ Cellulose Gum.

The solution of carboxyalkyl cellulose and water suitably comprises from about 0.01 to about 90 weight  
percent, beneficially from about 0.01 to about 30 weight percent, and preferably from about 2 to about 25  
weight percent of carboxyalkyl cellulose based on total solution weight. The carboxyalkyl cellulose is

suitably dissolved in a solvent comprising at least about 30 weight percent water, beneficially about 50 weight percent water, preferably about 75 weight percent water, and most preferably about 100 weight percent water. When a co-solvent is employed with the water, other suitable solvents include methanol, ethanol, and acetone.

5 The solution of carboxyalkyl cellulose and water and the recovered carboxyalkyl cellulose may be acidic, neutral, or slightly basic. As used herein, acidity will be stated in terms of the degree of molar acidification (DA). The degree of molar acidification is defined as the number of free-acid, carboxyl groups divided by the total number of carboxyl groups, either free-acid or salt-form. The degree of molar acidification is suitably less than 0.07, preferably less than about 0.05, assuming use of an essentially  
10 completely neutralized carboxyalkyl cellulose having few free acid groups and little, if any, residual base. The solution of carboxyalkyl cellulose and water can be acidified by the addition of an aqueous solution of an inorganic acid such as hydrochloric acid, nitric acid, etc. or an aqueous solution of an organic acid, such as acetic acid, or the like.

If it is desired to provide the solution of carboxyalkyl cellulose and water with a basic pH, a base such  
15 as an aqueous solution of sodium hydroxide, potassium hydroxide, ammonia, or the like can be added to the solution.

The solution of carboxyalkyl cellulose and water will suitably have a pH within the range of from about 5.0 to about 11.0, beneficially from about 6.0 to about 10.0, and preferably from about 6.5 to about 9. The recovered carboxyalkyl cellulose will generally have the same pH as the solution. However, Applicants have  
20 noted that when the carboxyalkyl cellulose is recovered by evaporative drying, the evaporative drying step tends to lower the pH of the carboxyalkyl cellulose solution if it is initially basic.

When the carboxyalkyl cellulose of the present invention is intended for use in personal care products such as diapers, training pants, feminine care products, and the like, it is generally desired that the carboxyalkyl cellulose have a generally neutral character. For this reason, it is generally preferred that the  
25 solution of carboxyalkyl cellulose and water be formed with a generally neutral pH. Alternatively, if the solution of carboxyalkyl cellulose and water is formed with an acidic or basic pH, the recovered carboxyalkyl cellulose may be neutralized. For example, if the solution is acidic, the recovered carboxyalkyl cellulose will be acidic. The recovered carboxyalkyl cellulose may be neutralized, for example, by contacting with a gaseous base such as ammonia.

30 The solution of carboxyalkyl cellulose and water can be formed at any temperature at which the carboxyalkyl cellulose is soluble in the water. Generally, such temperatures will be within the range of from about 10°C to about 100°C. As a general rule, it is preferred to form the solution of carboxyalkyl cellulose with agitation.

After forming the solution of carboxyalkyl cellulose and water, the carboxyalkyl cellulose is recovered  
35 from the solution. Any method of recovering the carboxyalkyl cellulose from the solution, without unacceptably deteriorating the absorption characteristics of the carboxyalkyl cellulose, is suitable for use in the present invention. Examples of such methods include evaporative drying, freeze drying, precipitation, critical point drying, and the like.

As a general rule, the carboxyalkyl cellulose can be recovered by evaporative drying at a temperature  
40 within the range from of about 10°C to about 100°C, preferably from about 50°C to about 80°C. Naturally, higher temperatures can be employed if the solution is placed under pressure. Lower temperatures can be employed if the solution is placed under a vacuum.

Other methods of recovery include precipitation in which a precipitating agent, such as methanol, ethanol or acetone is added to the solution of carboxyalkyl cellulose and water to precipitate the  
45 carboxyalkyl cellulose out of solution. The carboxyalkyl cellulose can then be recovered by filtration. If precipitation is used to recover the carboxyalkyl cellulose, it may be desirable to wash the recovered carboxyalkyl cellulose to remove the precipitating agent.

Depending on the form in which the carboxyalkyl cellulose is recovered, it may be necessary or desirable to alter the form of the carboxyalkyl cellulose. For example, if evaporative drying is employed, the  
50 carboxyalkyl cellulose may be recovered in the form of a film or sheet. It may be desirable to comminute the film or sheet material into particles or flakes of material.

The form of the carboxyalkyl cellulose desired will depend to a large extent on the use for which it is intended. When the carboxyalkyl cellulose is intended for use in absorbent personal care products, it is generally desired that the carboxyalkyl cellulose be in the form of a discrete particle, fiber or flake. When in  
55 the form of a particle, it is generally desired that the particle have a maximum cross-sectional diameter within the range from about 50 µm to about 2,000 µm, preferably within the range from about 100 µm to about 1,000 µm, most preferably within the range from about 300 µm to about 600 µm.

The recovered carboxyalkyl cellulose is then heat-treated at an elevated temperature to crosslink the carboxyalkyl cellulose. As a general rule, any combination of temperature and time which achieves a desired degree of crosslinking, without undesirable damage to the carboxyalkyl cellulose, is suitable for use in the present invention. As a general rule, the carboxyalkyl cellulose will be heat-treated at a temperature within the range from about 100° C to about 250° C, beneficially from about 120° C to about 200° C, and preferably from about 130° C to about 170° C.

The higher the temperature employed, the shorter the period of time necessary to achieve the desired degree of crosslinking. Generally, the heat-treating process will extend over a time period within the range of from about 1 to about 600 min, beneficially from about 1 to about 120 min, and preferably from about 5 to about 60 min.

The inventors found that, by providing the solution of carboxyalkyl cellulose and water with an acidic character, the time necessary to effect the heat-treatment can be shortened. Providing the solution of carboxyalkyl cellulose and water with a slightly basic character tends to lengthen the time of the heat-treating process, at a given temperature, compared to a slightly acidic or neutral solution of carboxyalkyl cellulose and water. Nonetheless, similar general absorptive properties can be achieved with either an acidic, neutral, or slightly basic carboxyalkyl cellulose. In some instances, it may be desired to provide the solution of carboxyalkyl cellulose and the recovered carboxyalkyl cellulose with an acidic character in order to lower the temperature or shorten the time of the heat treatment. In this instance, the carboxyalkyl cellulose is desirably neutralized after the heat-treatment step.

The heat-treating process causes the carboxyalkyl cellulose to cross link and become generally water-insoluble. The heat-treating process desirably produces a carboxyalkyl cellulose having the ability to absorb a liquid while the carboxyalkyl cellulose is under a load. Synthetic polymeric materials, such as polyacrylates, having a generally high ability to absorb while under a load have been found to minimize the occurrence of gel-blocking when incorporated in absorbent products. The method by which the Absorbency Under Load is determined is set forth below in connection with the examples. The Absorbency Under Load values determined as set forth below and reported herein refer to the amount, in grams, of an aqueous solution containing 0.9 weight percent sodium chloride a gram of the carboxyalkyl cellulose (carboxyalkyl polysaccharide) can absorb in 60 min under a load of about 0.3 pounds per square inch. As a general rule, it is desired that the carboxyalkyl cellulose of the present invention have an Absorbency Under Load (AUL) of at least about 17, beneficially of at least about 20, most beneficially of at least about 24, and preferably of at least about 27 grams per gram.

Further, the carboxyalkyl cellulose of the present invention suitably has a Free-Swell Capacity of at least about 20 grams, preferably of at least about 30 grams, and most preferably of at least about 35 grams. Free-Swell Capacity refers to the amount, in grams, of an aqueous solution containing 0.9 weight percent sodium chloride the carboxyalkyl cellulose can absorb in 60 min under no load. The exact procedure by which the Free-Swell Capacity is determined is set forth below in connection with the examples.

Any combination of time and temperature which produces a crosslinked carboxyalkyl cellulose having the described Absorbency Under Load and Free-Swell capacity is preferred for use in the present invention. The inventors have found that there is generally an optimum combination of time and temperature at which to crosslink and optimize the Absorbency Under Load and Free-Swell Capacity of a particular carboxyalkyl cellulose material. If too little crosslinking occurs, the carboxyalkyl cellulose may possess a high Free-Swell Capacity but a relatively low Absorbency Under Load. If too much crosslinking occurs, the carboxyalkyl cellulose may have a relatively low Free-Swell Capacity and a relatively low Absorbency Under Load due to the inability of the carboxyalkyl cellulose to absorb much liquid.

The inventors found that solubilizing the carboxyalkyl cellulose in an aqueous solution and recovering prior to crosslinking produces a carboxyalkyl cellulose suitable for further crosslinking into materials having improved absorption properties. For example, a standard carboxymethyl cellulose heat-treated at 150° C for 60 min has an Absorbency Under Load of 6.4 grams and remains water soluble. When the same carboxymethyl cellulose is solubilized in water, recovered by evaporative drying and heat-treated at 150° C for 60 min, the carboxymethyl cellulose has an Absorbency Under Load of 24.8.

The inventors hypothesize that the solubilization may allow a molecular rearrangement of the carboxyalkyl cellulose which produces a more uniform distribution of the carboxyl groups and hydroxyl groups within the carboxyalkyl cellulose material. The more uniform distribution of the carboxyl groups within the carboxyalkyl cellulose may result in a more uniform crosslinking as a result of the heat-treatment step.

The inventors are uncertain as to whether or not the crosslinking which occurs is a chemical crosslinking, a physical crosslinking caused by the formation of crystal structures, or a combination of chemical and physical crosslinking. The exact cause of the improved absorbent properties achieved by the

method of the present invention is not important so long as the improved absorbent properties are achieved.

In another aspect, the present invention relates to a water-swellaable, generally water-insoluble carboxyalkyl polysaccharide characterized in that it has an average degree of substitution of from about 0.3 to about 1.5 and has an Absorbency Under Load value of at least about 17 and a Free-Swell Capacity of at least about 20 grams per gram. Such a carboxyalkyl polysaccharide is suitably formed by the method described above. Nonetheless, the described method is not intended to be the exclusive method by which such a carboxyalkyl polysaccharide can be formed.

As described above, the carboxyalkyl polysaccharide is suitably a carboxyalkyl cellulose such as carboxymethyl cellulose, carboxyethyl cellulose, or the like. The carboxyalkyl cellulose has an Absorbency Under Load value of at least 17, beneficially of at least about 20, preferably of at least 24, and most preferably of at least about 27. The carboxyalkyl cellulose has a Free-Swell Capacity of at least about 20, beneficially of at least about 30, and preferably of at least 35.

The carboxyalkyl polysaccharides of the present invention are suitable for use in personal care products such as diapers, training pants, feminine care products, adult incontinent products, wound dressings, and the like.

#### Test Methods

##### 20 Absorbency Under Load

The Absorbency Under Load (AUL) is a test which measures the ability of an absorbent material to absorb a liquid (0.9 weight percent solution of sodium chloride in distilled water) while under an applied load or restraining force.

Referring to Fig. 1, the apparatus and method for determining AUL will be described. Shown is a perspective view of the apparatus in position during a test. Shown is a laboratory jack 1 having an adjustable knob 2 for raising and lowering the platform 3. A laboratory stand 4 supports a spring 5 connected to a modified thickness meter probe 6, which passes through the housing 7 of the meter, which is rigidly supported by the laboratory stand. A plastic sample cup 8, which contains the superabsorbent material sample to be tested, has a liquid-permeable bottom and rests within a Petri dish 9, which contains the saline solution to be absorbed. A weight 10 rests on top of a spacer disc (not visible) resting on top of the superabsorbent material sample (not visible).

The sample cup consists of a plastic cylinder having a 1 inch inside diameter and an outside diameter of 1.25 inch. The bottom of the sample cup is formed by adhering a metal screen having 150  $\mu\text{m}$  openings (100 mesh) to the end of the cylinder by heating the screen above the melting point of the plastic and pressing the plastic cylinder against the hot screen to melt the plastic and bond the screen to the plastic cylinder.

The modified thickness meter used to measure the expansion of the sample while absorbing the saline solution is a Mitutoyo Digimatic Indicator, IDC Series 543, Model 543-180, having a range of 0-0.5 inch and an accuracy of 0.00005 inch (Mitutoyo Corporation, 31-19, Shiba 5-chome, Minato-ku, Tokyo 108, Japan). As supplied from Mitutoyo Corporation, the thickness meter contains a spring attached to the probe within the meter housing. This spring is removed to provide a free falling probe, which has a downward force of about 27 grams. In addition, the cap over the top of the probe located on the top of the meter housing is also removed to enable attachment of the probe to the suspension spring 5 (available from McMaster-Carr Supply Co., Chicago, Illinois, Item No. 9640K41), which serves to counter or reduce the downward force of the probe to about 1 gram,  $\pm$  0.5 gram. A wire hook can be glued to the top of the probe for attachment to the suspension spring. The bottom tip of the probe is also provided with an extension needle (Mitutoyo Corporation, Part No. 131279) to enable the probe to be inserted into the sample cup.

To carry out the test, a 0.160 gram sample of the absorbent material, which has been sieved to a particle size between 300 and 600  $\mu\text{m}$ , is placed into the sample cup. The sample is then covered with a plastic spacer disc, weighing 4.4 grams, which is slightly smaller than the inside diameter of the sample cup and serves to protect the sample from being disturbed during the test. The 100 grams weight is then placed on top of the spacer disc, thereby applying a load of 0.3 pounds per square inch. The sample cup is placed in the Petri dish on the platform of the laboratory jack raised up until it contacts the tip of the probe. The meter is zeroed. A sufficient amount of saline solution is added to the Petri dish (50-100 milliliters) to begin the test. The distance the weight is raised by the expanding sample as it absorbs the saline solution is measured by the probe. This distance, multiplied by the cross-sectional area inside the sample cup, is a measure of the expansion volume of the sample due to absorption. Factoring in the density of the saline

solution and the weight of the sample, the amount of saline solution absorbed is readily calculated. The weight of saline solution absorbed after 60 min is the AUL value, expressed as grams saline solution absorbed per gram of absorbent. If desired, the readings of the modified thickness meter can be continuously input to a computer (Mitutoyo Digimatic Miniprocessor DP-2 DX) to make the calculations and provide AUL readings. As a cross-check, the AUL can also be determined by determining the weight difference between the sample cup before and after the test, the weight difference being the amount of solution absorbed by the sample.

#### Free-Swell Capacity

The Free-Swell Capacity for a given absorbent material is determined in the same manner as the Absorbency Under Load, with the exception that the 100 gram weight is not placed on top of the spacer disc. The Free-Swell Capacity is reported as the weight of the saline solution absorbed after 60 min, expressed as grams of saline absorbed per gram of absorbent.

#### Examples

##### Example 1.

A sodium carboxymethyl cellulose commercially available from the Aqualon Company under the trade designation Aqualon™ Cellulose Gum CMC-7HCF or CMC-7H4F is provided. The carboxymethyl cellulose has an average degree of substitution of 0.7. CMC-7H4F has a slightly higher molecular weight than the CMC-7HCF. The carboxymethyl cellulose is dissolved in distilled water to form a solution containing 2 weight percent carboxymethyl cellulose based on total solution weight. The solution is then either left at a neutral pH, slightly acidified through the addition of hydrochloric acid (0.1 molar aqueous solution) or made basic by the addition of sodium hydroxide (0.1 molar aqueous solution). The carboxymethyl cellulose is recovered from the solution by evaporative drying at 80°C in a Blue M air-convection oven. After drying, the recovered carboxymethyl cellulose is ground into granules in a blender and heat-treated at various times and temperatures in an oven. Various combinations of temperature, time, and solution pH are made, and the physical properties of the resultant carboxymethyl cellulose determined. The exact process conditions and the physical properties of the resultant carboxymethyl cellulose are set forth in Table 1. Sample Nos. 1-38 employ the CMC-7HCF while Sample Nos. 39-45 employ the CMC-7H4F.

TABLE 1

Sample No.	pH (DA) <sup>1</sup>	Treatment		AUL <sup>2</sup> (g/g)	FSC <sup>3</sup> (g/g)
		Temp (°C)	Time (min)		
1*	6.08 (3)	N/A	N/A	9.7	
2	6.08 (3)	140	5	16.9	
3	6.08 (3)	140	8	15.5	
4	6.08 (3)	140	10	14.9	
5	6.08 (3)	140	20	12.6	
6	6.08 (3)	140	30	10.8	
7*	6.44 (0.5)	N/A	N/A	6.4	
8	6.44 (0.5)	120	60	19.3	
9	6.44 (0.5)	140	10	16.1	
10	6.44 (0.5)	140	20	20.0	
11	6.44 (0.5)	140	30	20.0	
12	6.44 (0.5)	140	40	18.0	
13	6.44 (0.5)	140	50	16.8	
14	6.44 (0.5)	150	10	17.8	
15	6.44 (0.5)	150	15	20.0	
16	6.44 (0.5)	150	20	19.9	
17	6.44 (0.5)	150	30	15.2	
18*	7.4 (0)	N/A	N/A	7.1	
19	7.4 (0)	130	90	22.2	
20	7.4 (0)	150	30	21.4	46.5
21	7.4 (0)	150	40	25.3	
22	7.4 (0)	150	45	27.1	44.6
23	7.4 (0)	150	50	26.1	
24	7.4 (0)	150	60	24.8	43.7



Sample No.	pH (DA) <sup>1</sup>	Treatment Temp (°C)	Treatment Time (min)	AUL <sup>2</sup> (g/g)	FSC <sup>3</sup> (g/g)
25	7.4 (0)	150	75	23.7	
5 26	7.4 (0)	150	90	21.6	34.8
27	7.4 (0)	150	120	19.2	29.6
28*	8.92	N/A	N/A	7.0	
10 29	8.92	150	40	17.1	
30	8.92	150	80	21.8	
31	8.92	150	100	20.9	
15 32	8.92	150	120	21.6	
33	8.92	150	150	18.6	
34*	10.72	N/A	N/A	6.6	
35	10.72	150	50	11.6	
20 36	10.72	150	100	19.3	
37	10.72	150	150	20.4	
38	10.72	150	200	15.9	
25 39*	0	N/A	N/A	8.1	
40	0	150	8	27.4	
41	0	150	10	27.7	
42	0	150	12	27.8	
30 43	0	150	15	27.0	
44	0	150	20	27.4	
45 45	0	150	60	18.5	

N/A = Not applicable

\* Not an example of the present invention

<sup>1</sup> pH of the solution of carboxymethyl cellulose and water prior to recovery (Degree of Molar Acidification)

<sup>2</sup> Absorbency Under Load in grams absorbed aqueous saline solution (0.9 weight percent) per gram of carboxymethyl cellulose under a load of 0.3 psi.

<sup>3</sup> Free Swell Capacity in grams absorbed aqueous saline solution (0.9 weight percent) per gram of carboxymethyl cellulose.

#### Example 2.

Example 1 is repeated with the exception that a sodium carboxymethyl cellulose commercially available from the Aqualon Company under the trade designation Aqualon® Cellulose Gum CMC-9H4 is employed. The carboxymethyl cellulose has an average degree of substitution of 0.9. Again, the exact process conditions and physical properties of the resultant carboxymethyl cellulose are set forth in Table 2.

TABLE 2

Sample No.	DA (mol%) <sup>1</sup>	Treatment Temp (°C)	Treatment Time (min)	AUL <sup>2</sup> (g/g)	FSC <sup>3</sup> (g/g)
46	3	150	30	10.5	
47*	0.5	N/A	N/A	7.2	
48	0.5	150	5	17.9	
49	0.5	150	8	22	
50	0.5	150	10	22.3	
51	0.5	150	15	20.5	
52	0.5	150	20	18.3	
53	0.5	150	30	16	
54*	0.1	N/A	N/A	6.9	
55	0.1	150	10	10.7	
56	0.1	150	20	22.1	
57	0.1	150	30	22.2	
58	0.1	150	40	20.4	
59	0.1	150	60	18.8	
60*	0	N/A	N/A	7.4	
61	0	130	60	8.7	
62	0	130	90	15.8	
63	0	130	120	20.3	
64	0	130	150	22.8	
65	0	N/A	N/A	7.4	
66	0	170	10	19.8	
67	0	170	20	13.3	
68	0	170	30	10.5	
N/A = Not Applicable					

\* Not an example of the present invention

<sup>1</sup> Degree of Molar Acidification

<sup>2</sup> Absorbency Under Load in grams absorbed aqueous saline solution (0.9 weight percent) per gram of carboxymethyl cellulose under a load of 0.3 psi.

<sup>3</sup> Free Swell Capacity in grams absorbed aqueous saline solution (0.9 weight percent) per gram of carboxymethyl cellulose.

### Example 3

Example 2 is repeated with the exception that the carboxymethyl cellulose is recovered and comminuted to form both granules and flakes. The carboxymethyl cellulose is then heat-treated at 150°C for various times to determine the effect of geometry on the heat-treatment process. The results are set forth in Table 3. Samples 69-73 are in granular form. Samples 74-80 are in the form of flakes.

TABLE 3

Sample No.	DA (mol%) <sup>1</sup>	Treatment Temp (* C)	Treatment Time (min)	AUL <sup>2</sup> (g/g)
69*	0	N/A	N/A	7.4
70	0	150	20	19
71	0	150	30	24
72	0	150	40	24.5
73	0	150	50	22.4
74*	0	N/A	N/A	7.4
75	0	150	10	9.8
76	0	150	15	15.8
77	0	150	20	25
78	0	150	30	23
79	0	150	45	20.8
80	0	150	60	18.4
N/A = Not Applicable				

\* Not an example of the present invention

<sup>1</sup> Degree of Molar Acidification

<sup>2</sup> Absorbency Under Load in grams absorbed aqueous saline solution (0.9 weight percent) per gram of carboxymethyl cellulose under a load of 0.3 psi.

#### Example 4

Example 2 is repeated with the exception that the carboxymethyl cellulose is dissolved in distilled water to form a solution containing 23 weight percent carboxymethyl cellulose based on total solution weight. The recovered carboxymethyl cellulose is heat-treated in the form of granules at 150 °C for various time periods. The physical properties of the resultant polymer are set forth in Table 4.

TABLE 4

Sample No.	DA (mol%) <sup>1</sup>	Treatment Temp (* C)	Treatment Time (min)	AUL <sup>2</sup> (g/g)
81*	0	N/A	N/A	7.3
82	0	150	20	22
83	0	150	30	22.2
84	0	150	40	20.5
N/A = Not Applicable				

\* Not an example of the present invention

<sup>1</sup> Degree of Molar Acidification

<sup>2</sup> Absorbency Under Load in grams absorbed aqueous saline solution (0.9 weight percent) per gram of carboxymethyl cellulose under a load of 0.3 psi.

Control samples of the carboxymethyl cellulose of Example 1 and Example 2 in which the carboxymethyl cellulose is subjected to a heat-treatment process without having been dissolved in an aqueous solution and recovered were performed. Again, the exact process conditions of the heat-treatment step and the physical properties of the resultant polymer are set forth in Table 5. Both control samples remain water soluble even after the heat-treatment step.

TABLE 5

Sample No.	Treatment Temp (°C)	Treatment Time (min)	AUL(g/g)
85*	150	15	6.8
86*	150	60	6.4

\* Not an example of the present invention

Fig. 2 illustrates the Absorbency Under Load of the carboxymethyl cellulose of Example 1 heat-treated at a temperature of 150°C for various lengths of time. It is noted that the optimum heat-treatment time appears to be approximately 45 min, producing an absorbent carboxymethyl cellulose having an Absorbency Under Load of about 27.

Fig. 3 illustrates the effect of time of heat-treatment on Absorbency Under Load values and Free-Swell Capacity as a function of treatment time at 150°C. As can be seen from reference to Fig. 3, an optimum treatment time can be determined.

Fig. 4 illustrates the effect of the initial pH of the solution of carboxymethyl cellulose and water on the Absorbency Under Load of carboxymethyl celluloses treated at 150°C for various periods of time. As can be seen from reference to Fig. 4, varying the initial pH of the solution of carboxymethyl cellulose and water alters the optimum treatment time. As a general rule, the lower the pH, the shorter the treatment time to optimize absorbent properties.

Fig. 5 shows the effect of temperature of heat-treatment on the Absorbency Under Load values of carboxymethyl cellulose of a slightly acidified system (0.5 DA). As can be seen from reference to Fig. 5, the higher the treatment temperature, the shorter the time necessary to obtain the optimum Absorbency Under Load value.

Fig. 6 illustrates the Absorbency Under Load value of the carboxymethyl cellulose of Example 3 heat-treated at 150°C for various times. Again, as can be seen from reference to Fig. 6, an optimum heat-treatment time can be determined. In the case of Fig. 6, the optimum time is about 20 minutes.

Fig. 7 illustrates the effect of the degree of molar acidification on the carboxymethyl cellulose of Examples 2 and 3. As can be seen from reference to Fig. 7, the more acidic the carboxymethyl cellulose, the shorter the time necessary to achieve the optimum Absorbency Under Load value.

Fig. 8 illustrates the effect of temperature of the heat-treatment process on the Absorbency Under Load performance of the carboxymethyl cellulose of Examples 2 and 3. Again, it is seen that as the temperature of heat-treatment increases, the time necessary to achieve the optimum Absorbency Under Load value decreases.

Fig. 9 illustrates the effect of the geometry of the carboxymethyl cellulose on the Absorbency Under Load performance. As can be seen from reference to Fig. 9, carboxymethyl cellulose in the form of flakes tends to reach the optimum Absorbency Under Load value faster.

Fig. 10 illustrates the effect of the concentration of carboxymethyl cellulose in the initial solution of carboxymethyl cellulose and water. Reference to Fig. 10 shows that, at higher concentrations of carboxymethyl cellulose, lower maximum Absorbency Under Load values are achieved, but that such values are achieved faster than at lower concentrations.

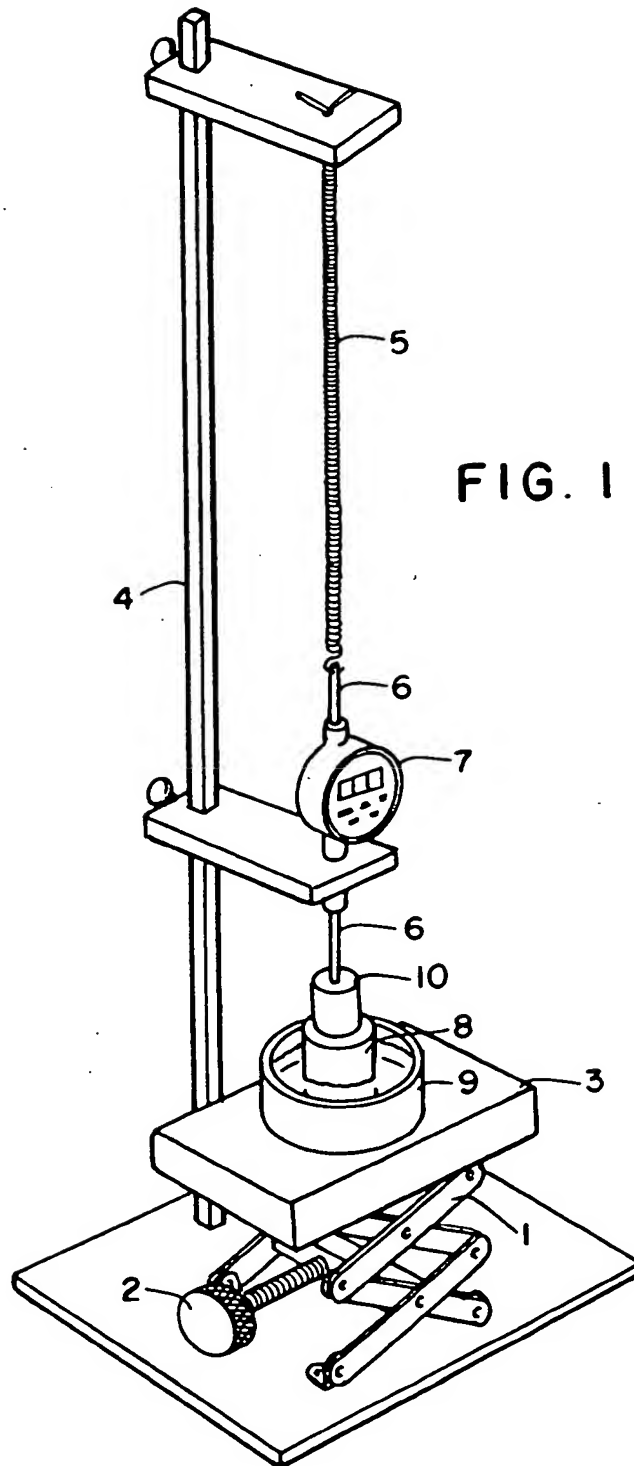
While the present invention has been described in terms of the specific embodiments described above, numerous equivalent changes and modifications will be clear to those skilled in the art. Accordingly, the specific examples set forth above are not intended to limit, in any manner, the scope of the invention as set forth in the appended claims.

#### Claims

1. A method for producing a water-swellable, water-insoluble carboxyalkyl polysaccharide, characterized by the following steps:  
forming a solution comprising a water-soluble carboxyalkyl polysaccharide and water, said carboxyalkyl polysaccharide having an average degree of substitution from about 0.3 to about 1.5;  
recovering said carboxyalkyl polysaccharide from said solution; and  
heat-treating said recovered carboxyalkyl polysaccharide at a temperature and for a time sufficient to crosslink said carboxyalkyl polysaccharide to render said carboxyalkyl polysaccharide generally water insoluble.

2. The method according to claim 1 wherein the carboxyalkyl polysaccharide is a carboxyalkyl cellulose.
3. The method according to claim 1 or 2, wherein the solution comprises from about 0.01 to about 90 weight percent of said carboxyalkyl polysaccharide.
- 5 4. The method according to claim 2 or 3, wherein said carboxyalkyl cellulose has a degree of substitution of from about 0.4 to about 1.2.
- 10 5. The method according to any of claims 1 to 4, wherein said solution comprising said carboxyalkyl polysaccharide and water has a degree of acidification of less than 0.07.
6. The method according to any of claims 1 to 5, wherein said solution comprising said carboxyalkyl polysaccharide and water has a generally neutral pH.
- 15 7. The method according to any of claims 1 to 5, wherein said solution comprising said carboxyalkyl polysaccharide and water is basic.
8. The method according to any of claims 1 to 7, particularly of claim 2, wherein said carboxyalkyl cellulose is carboxymethyl cellulose.
- 20 9. The method according to any of claims 1 to 8, wherein said carboxyalkyl polysaccharide is recovered from said solution by evaporative drying.
- 25 10. The method according to any of claims 1 to 8, wherein said carboxyalkyl polysaccharide is recovered from said solution by precipitation.
- 30 11. The method according to any of claims 2 to 10, particularly of claim 2, wherein said recovered carboxyalkyl cellulose is heat-treated at a temperature and for a time sufficient to provide said carboxyalkyl cellulose with an Absorbency Under Load of at least about 17.
- 35 12. The method according to claim 11, wherein said Absorbency Under Load is at least about 24.
13. The method according to claim 11, wherein said Absorbency Under Load is at least about 27.
- 40 14. The method according to any of claims 11 to 13, wherein said carboxyalkyl cellulose is heat-treated at a temperature of from about 120 °C to about 200 °C for a time of from about 1 min. to about 120 mins.
15. The method according to claim 14, wherein said carboxyalkyl cellulose is heat-treated at a temperature of from about 130 °C to about 170 °C for a time of from about 1 min. to about 120 min.
- 45 16. The method according to claim 15, wherein said carboxyalkyl cellulose is heat-treated at a temperature of from about 130 °C to about 170 °C for a time of from about 5 min. to about 60 min.
17. The method according to any of claims 1 to 16, further comprising the step of comminuting said carboxyalkyl polysaccharide after recovery and before heat-treating.
- 50 18. A method for producing a water-swellaable, generally water-insoluble carboxyalkyl polysaccharide, characterized by the following sequential steps:  
forming a solution comprising from about 0.01 to about 90 weight percent of a water-soluble carboxyalkyl polysaccharide, based on total solution weight and water, said carboxyalkyl polysaccharide having an average degree of substitution of from about 0.4 to about 1.2;  
recovering said carboxyalkyl polysaccharide from said solution; and  
heat-treating said recovered carboxyalkyl polysaccharide at a temperature of from about 100 °C to about 250 °C for a time of from about 1 min. to about 600 min. , such that said carboxyalkyl polysaccharide is rendered generally water-insoluble and has an Absorbency Under Load of at least about 17.
- 55 19. The method according to claim 18 wherein the carboxyalkyl polysaccharide is a carboxyalkyl cellulose.

20. A carboxyalkyl polysaccharide produced by the method of any of claims 1 to 19, particularly of claims 1, 18 and 19.
- 5 21. A water-swellaable, generally water-insoluble, carboxyalkyl polysaccharide characterized in that said carboxyalkyl polysaccharide has an average degree of substitution from about 0.3 to about 1.5 and has an Absorbency Under Load of at least about 17 and a Free-Swell Capacity of at least about 20.
22. The carboxyalkyl polysaccharide according to claim 21, wherein said carboxyalkyl polysaccharide has an Absorbency Under Load of at least about 20.
- 10 23. The carboxyalkyl polysaccharide according to claim 21, wherein said carboxyalkyl polysaccharide has an Absorbency Under Load of at least about 24.
24. The carboxyalkyl polysaccharide according to claim 21, wherein said carboxyalkyl polysaccharide has an Absorbency Under Load of at least about 27.
- 15 25. The carboxyalkyl polysaccharide according to any of claims 21 to 24, wherein said carboxyalkyl polysaccharide has a Degree of Molar Acidification of less than 0.07.
- 20 26. The carboxyalkyl polysaccharide according to any of claims 21 to 25, wherein said carboxyalkyl polysaccharide is generally neutral.
27. The carboxyalkyl polysaccharide according to any of claims 21 to 25, wherein said carboxyalkyl polysaccharide is basic.
- 25 28. The carboxyalkyl polysaccharide according to any of claims 21 to 27, wherein said carboxyalkyl polysaccharide is carboxyalkyl cellulose.
29. The carboxyalkyl cellulose according to claim 28, wherein said carboxyalkyl cellulose is carboxymethyl cellulose.
- 30 30. The carboxyalkyl polysaccharide according to claim 24, wherein said carboxyalkyl polysaccharide is carboxymethyl cellulose.
- 35 31. The carboxyalkyl cellulose according to claim 28, wherein said carboxyalkyl cellulose has a Free-Swell Capacity of at least about 30.
32. The carboxyalkyl cellulose according to claim 28, wherein said carboxyalkyl cellulose has a Free-Swell Capacity of at least about 35.
- 40 33. The carboxyalkyl polysaccharide according to any of claims 21 to 32, wherein said carboxyalkyl polysaccharide is in the form of discrete particles.
34. A water-swellaable, generally water-insoluble, carboxyalkyl polysaccharide characterized in that said carboxyalkyl polysaccharide has an average degree of substitution from about 0.4 to about 1.2 and has an Absorbency Under Load of at least about 20 and a Free-Swell Capacity of at least about 20.
- 45 35. Use of a carboxyalkyl polysaccharide according to any of claims 20 to 34 for producing absorbent products.
- 50



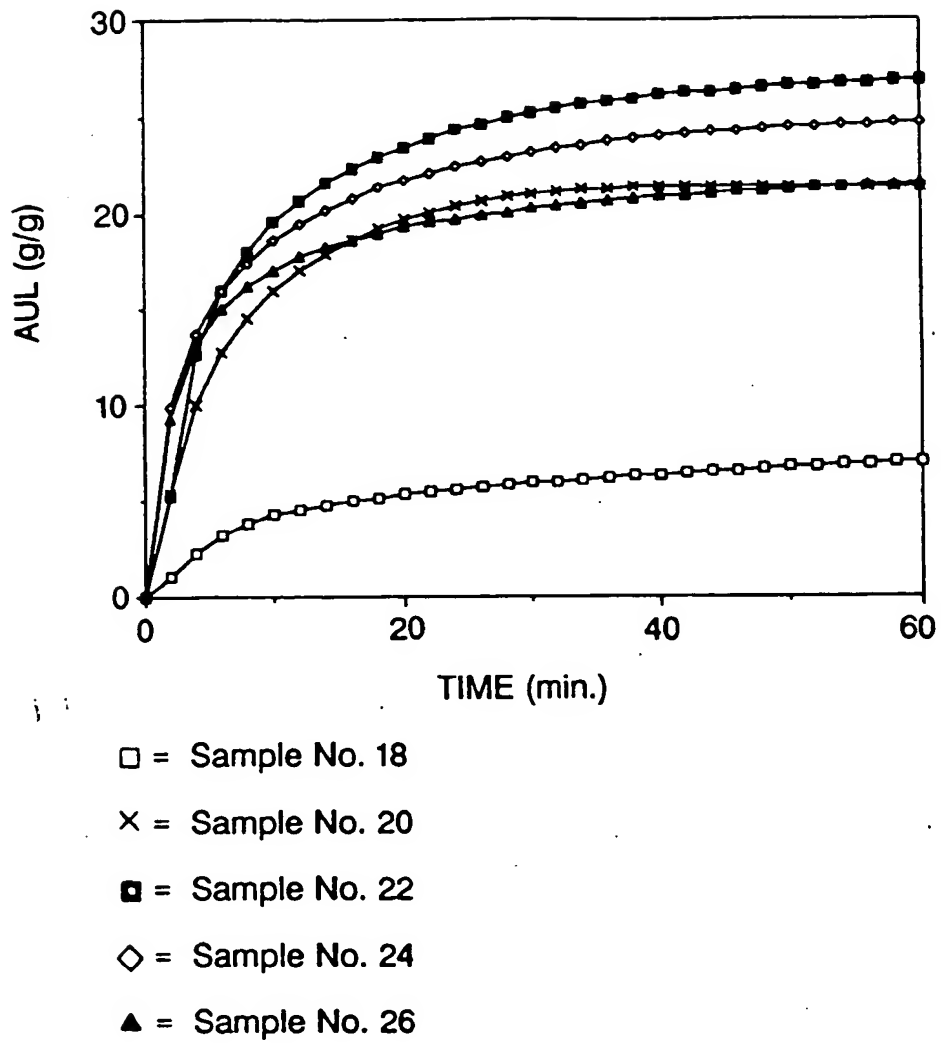
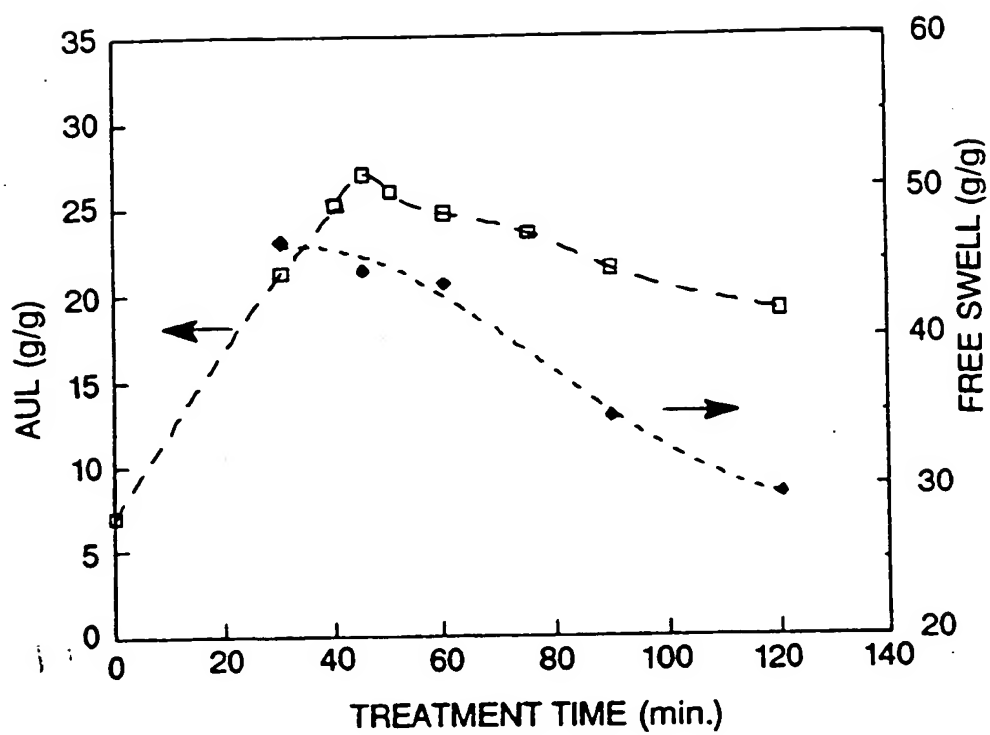


FIG. 2

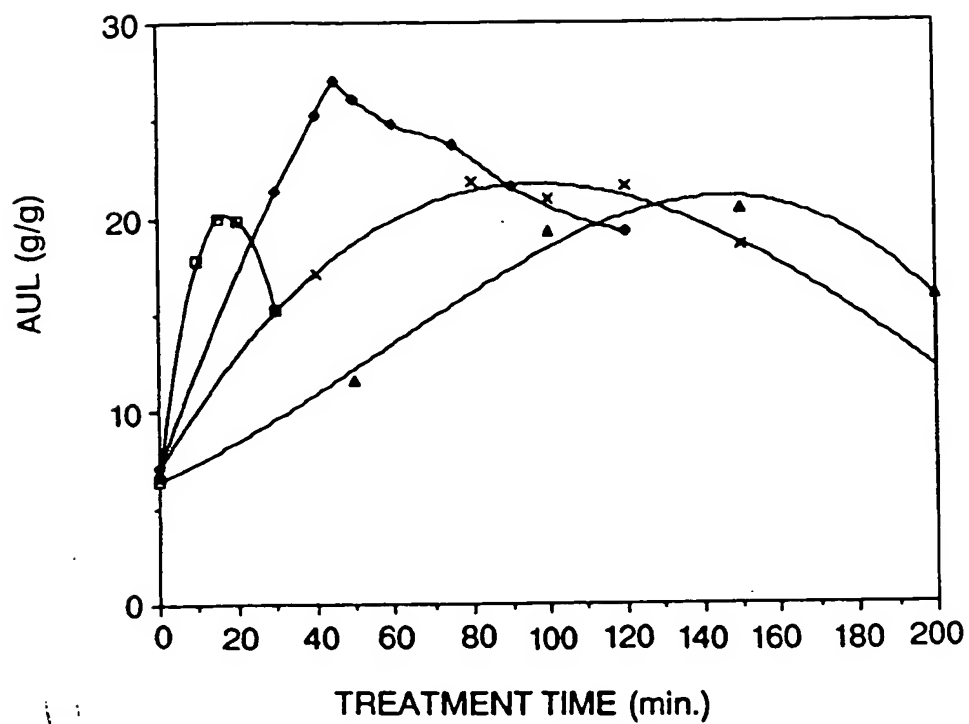




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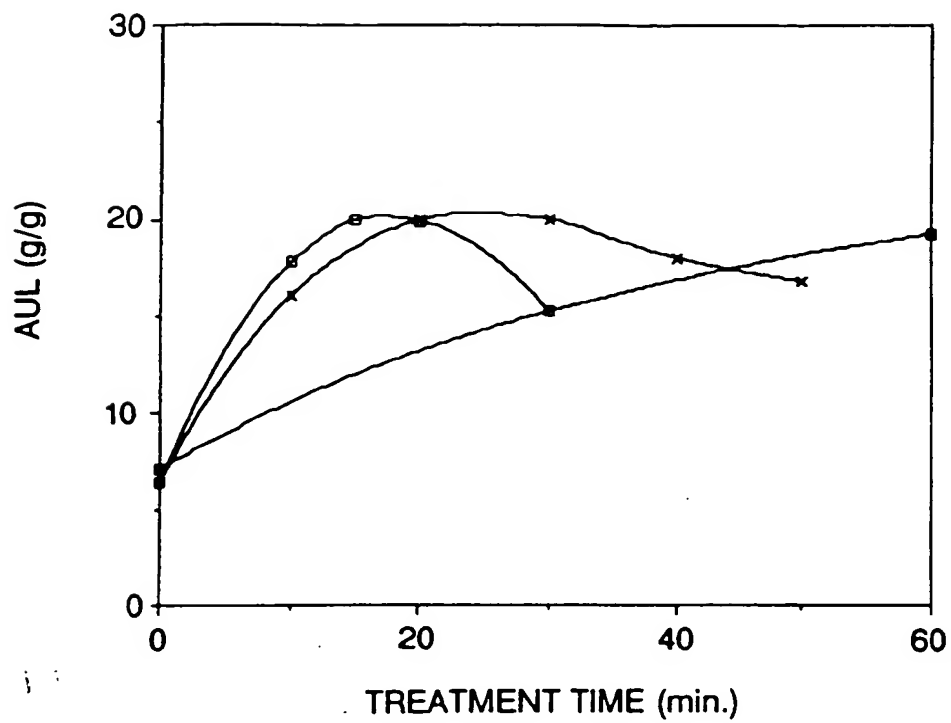
◆ = Sample No.'s 20, 22, 24, 26, 27

FIG. 3



- = Sample No.'s 7, 14, 15, 16, 17  
◆ = Sample No.'s 18, 20, 21, 22, 23, 24, 26, 27  
× = Sample No.'s 28, 29, 30, 31, 32, 33  
▲ = Sample No.'s 34, 35, 36, 37, 38

FIG. 4



■ = Sample No.'s 7, 8

× = Sample No.'s 7, 9, 10, 11, 12, 13

□ = Sample No.'s 7, 14, 15, 16, 17

FIG. 5

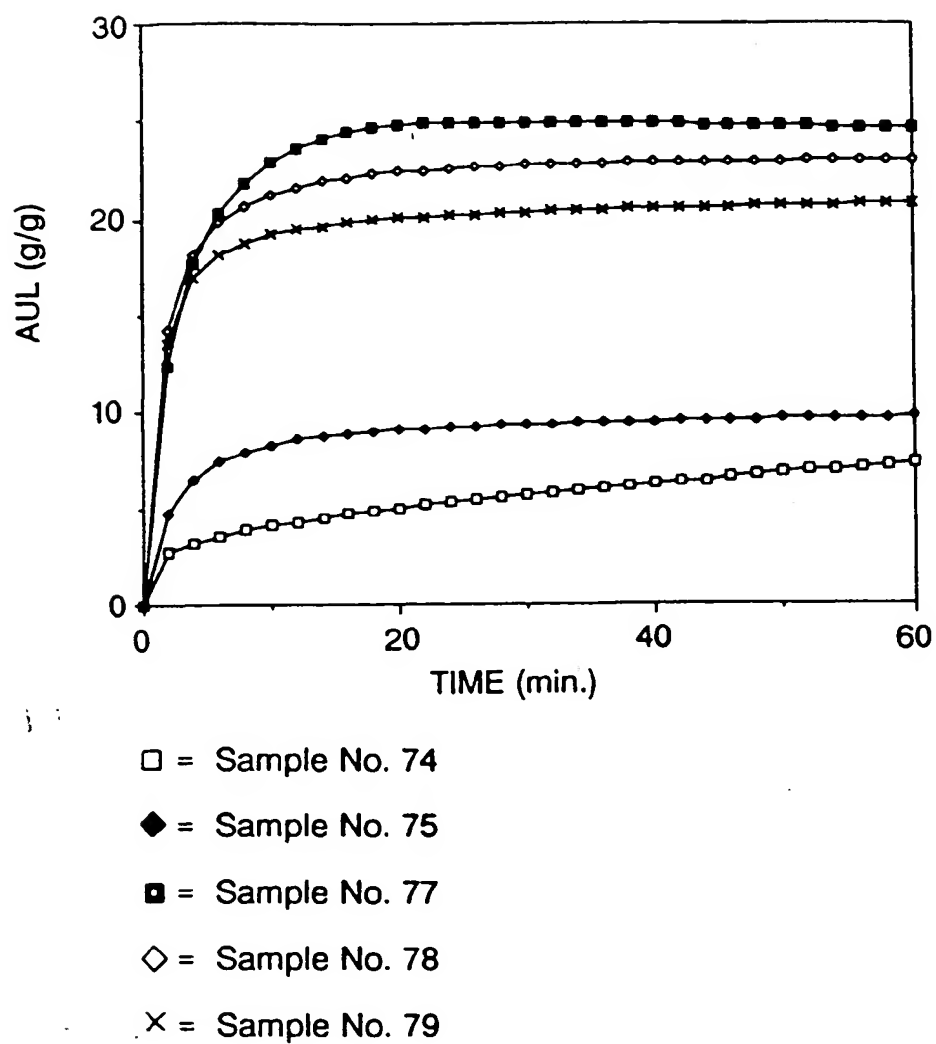
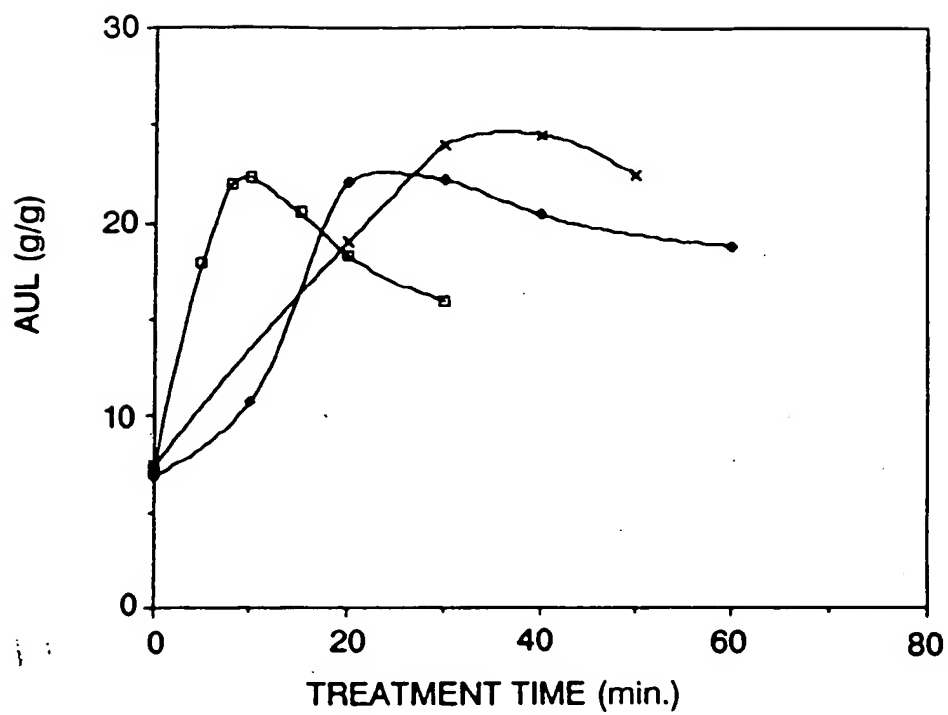


FIG. 6

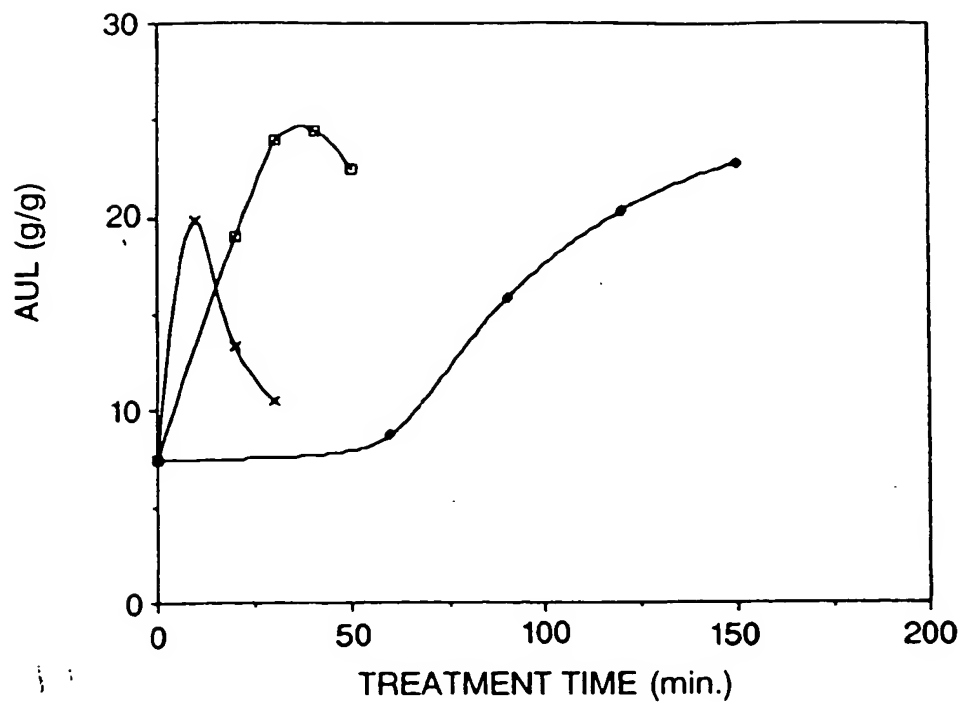


□ = Sample No.'s 47, 48, 49, 50, 51, 52, 53

◆ = Sample No.'s 54, 55, 56, 57, 58, 59

× = Sample No.'s 69, 70, 71, 72, 73

FIG. 7

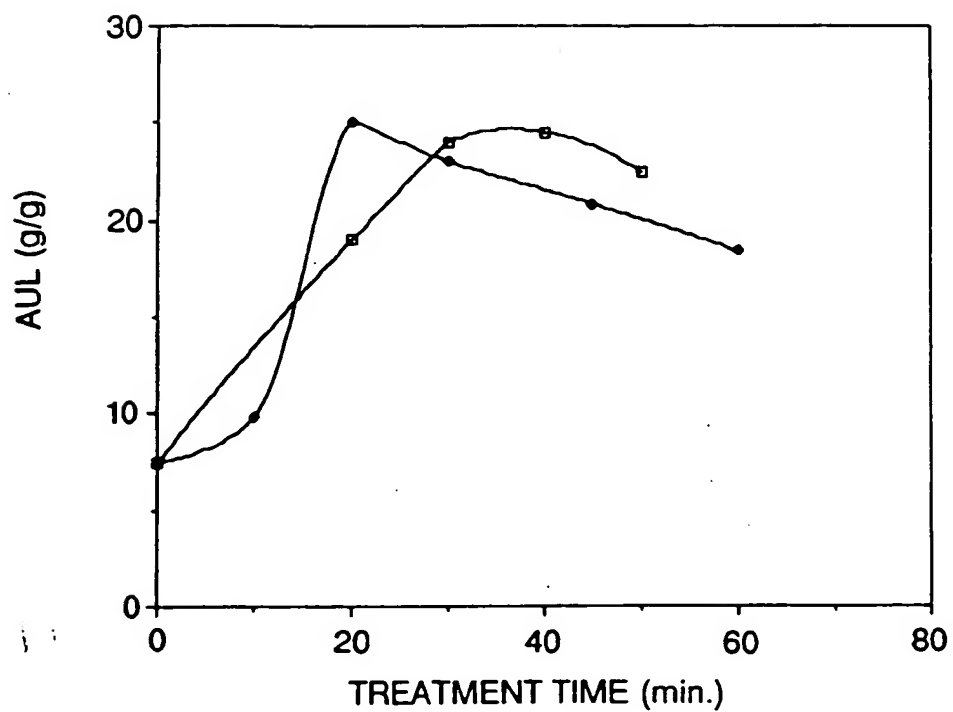


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□ = Sample No.'s 69, 70, 71, 72, 73

◆ = Sample No.'s 60, 61, 62, 63, 64

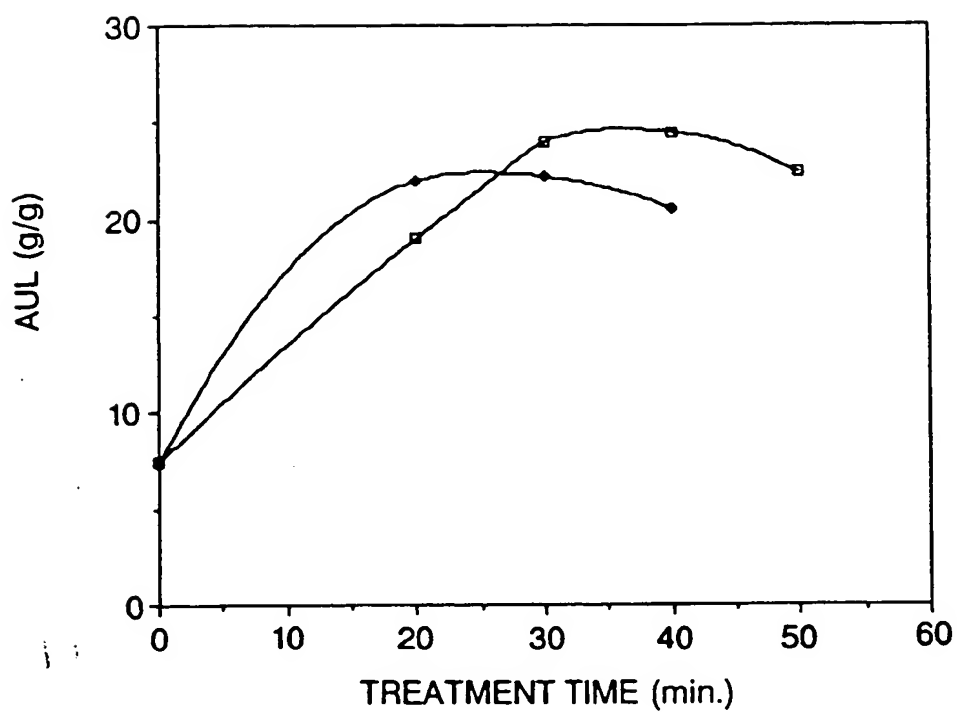
FIG. 8



□ = Sample No.'s 69, 70, 71, 72, 73

◆ = Sample No.'s 74, 75, 77, 78, 79, 80

FIG. 9



□ = Sample No.'s 69, 70, 71, 72, 73

◆ = Sample No.'s 81, 82, 83, 84

FIG. 10





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(54) Carboxyalkyl polysaccharides and process for their preparation.

(57) Disclosed is a method for producing a water-swelling, generally water-insoluble, carboxyalkyl polysaccharide having improved absorption properties. The method involves forming a solution of carboxyalkyl polysaccharide and water, recovering the carboxyalkyl polysaccharide from the solution and heat-treating said recovered carboxyalkyl polysaccharide. Also, described is a carboxyalkyl polysaccharide having improved absorption properties.

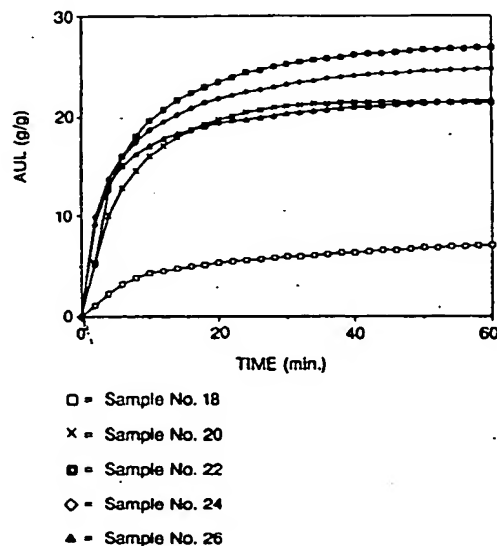


FIG. 2

EP 0 538 904 A3



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 92 11 8266

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	GB-A-1 086 323 (COURTAULDS LTD)  * the whole document * ---	1-5, 7-10, 18-20,35	C08B37/00 C08B11/20 C08B15/10 //A61L15/00
Y	FR-A-2 510 628 (PERSONAL PRODUCTS COMPANY)  * page 2, line 7 - line 23 * * page 3, line 32 - line 33 * * page 5, line 31 - line 33 * ---	1-4,8, 11-16, 18-24, 28-32, 34,35	
Y	US-A-3 858 585 (CHATTERJEE)  * column 1, line 11 - line 21 * * claims; examples * ---	1-4,8, 11-16, 18-24, 28-32, 34,35	
A	US-A-4 200 736 (SHINOHARA ET AL.)  * column 2, line 5 - line 16 * * table 1 * ---	1,2,4,8, 11,14, 15,16, 18-20,35	TECHNICAL FIELDS SEARCHED (Int. Cl.5)  C08B A61L
D,A	US-A-3 723 413 (CHATTERJEE ET AL.)  -----		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 06 AUGUST 1993	Examiner MAZET J.-F.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document  T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons  A : member of the same patent family, corresponding document			

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